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A CRITICAL REVIEW ON SOLID LUBRICANTS

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ABSTRACT

The reduction of the interfacial friction between two surfaces in relative motion is a prerequisite for the proper functioning of many systems, ranging from machine parts to human joints. While the lubrication of two contacting surfaces primarily aims at the reduction of friction and wear, either by a separation of the surfaces by means of a fluid film or by introducing a layer of low shear strength between them, additional requirements such as the environmental compatibility of a lubricant or the energy efficiency of tribological systems have become important during recent years. This paper is limited to a discussion of the solid lubricants which comprise probably the largest single area. Although methods of attaching a lubricating solid to a wearing surface are many and vary considerably, the end result is the same, that is, a low friction medium is deposited to reduce friction and wear between two relatively moving surfaces under essentially dry conditions.

Key words: Lubrication, Solid lubrication, Organic lubrication, Inorganic lubrication.

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1. INTRODUCTION

Methods for minimizing friction losses have a significant importance; mineral or synthetic oil based lubricants are the most popular solution to friction and wear related losses for many steady regime applications. Under optimal conditions, oils can significantly lower friction losses as well as minimize wear. To minimize losses, rubbing partners must be separated by a thin lubrication film and the speed of the mating parts must match the properties of the lubricating film. Under such conditions, surface asperities become elastic, which is called Elasto-Hydrodynamic Lubrication or EHL. Among many factors, the main parameter to achieve EHL is the viscosity of the lubricant; however, since many mechanisms work during the dynamic operation of moving parts at a variable speed, the optimal regime may not always be achieved using lubricating oils alone. If elasto-hydrodynamic regime is not reached, then the surfaces will be in direct contact with each other during operation, which is commonly referred as the boundary lubrication (BL) regime. Under a boundary lubrication regime, the reduction of wear can be accomplished via surface-interaction, extreme pressure (EP) additives. Chemisorption of EP additives to various surfaces followed by formation of molecular boundary layer is the most common process, which can reduce wear behavior in materials. The future of better wear-reducing additives has been suggested to follow two main

routes: (i) a traditional route focusing on molecular liquid additives which can interact with surfaces chemically to form protective films, or (ii) a non-traditional route involving solid, nanoparticle-based additives which can be present in the asperities regions to carry load and reduce friction and wear behavior. Concurrent with the recent shift to more environment-friendly technologies, interest in the application of nano powders (including ceramic) in lubricating oils has grown. However such particles are still not widely employed due to a general lack of understanding about their behavior under frictional pressure[1].

2. HISTORY

The use of lubricants probably dates back to the invention of the wheel. Since this early beginning, lubrication and the production of lubricating media have grown to be one of the largest industries in the world, yet from one-third to one-half of all the energy produced still is lost to friction. Until the early 1800's, animal fats and oils were the primary lubricant materials. Since the first oil well was drilled in Titusville in 1859, the technology of lubrication has advanced rapidly. During the mid-1930's new materials developed to improve petroleum oils were first marketed. These materials, called additives, were used to increase the load carrying ability, lubricity, corrosion protection, and thermal oxidative stability of oils.

Since the mid 1930's a strong trend has developed toward using higher and higher temperatures in moving parts. Since the petroleum oils could not adequately do the job at high temperatures, new synthetic lubricant materials were introduced. Temperatures now encountered in supersonic aircraft, spacecraft, and certain industrial applications are beyond the useful range of even the synthetic lubricants. One result of this trend has been the development and use of solid lubricants to attain the necessary lubrication of delicate parts at extreme temperatures and pressures.

Although the slippery feel and appearance of graphite and molybdenum disulfide have been known for centuries, their use as solid lubricants in the modern sense dates back only about 20 years. Graphite is known by many names, some of which are black lead, carbon minerals, carburet of iron, caryon noir, plumbago, potelot, reissblei, and silver lead. It was long confused with similar appearing minerals, particularly molybdenite (MoS2). Not until 1565 was it classified as a separate mineral, and in 1779 it was proved to be carbon when it was oxidized to carbon dioxide.

About 1564, the Borrowdale graphite mines in England began producing graphite for pencils. These early pencils were made by encasing slabs of cut graphite in slotted wooden dowels. The name "graphite" did not come into being until 1789, when Werner drew it from the Greek word *Graphein,* which means "to write."

The ore molybdenite (M0S2) was known to the early Greeks. It has often been confused with graphite and with lead. The name is derived from the Greek word meaning lead.

Molybdenum is widely distributed over the earth's crust in the form of molybdenite. The largest commercial source of the mineral is in Climax, Colo., where it is mined from granite containing the ore in a finely divided state. Molybdenum disulfide has a metallic luster and is blue-grey to black in color. Early pioneers traveling through the Climax area used pulverized rock to lubricate the wheels on their Conestoga wagons. This probably was one of the first uses of a molybdenum disulfide solid lubricant [2].

2.1. History of Solid Lubrication

Although the use of graphite as a lubricant probably dates back to the middle ages, the use of bonded solid lubricant materials of the type being discussed in this document is relatively new. The first United States patent covering these materials was issued in the middle 1940's. Patents covering bonded solid film lubricants usually are issued covering both the lubricating solid and the binder material, the binder being the media by which the lubricating solid is attached to the substrate. Today, approximately 200 patents cover solid lubricating materials and binders.

The first patent issued in this country covered phosphoric acid bonded graphite. The use of molybdenum disulfide as a lubricating solid also started in the 1940's. It is currently the most popular

material. A large variety of binder materials were evaluated in the early bonded film work, including such materials as corn syrup, asphalt base varnish, silicone base varnish, and glycerol. Binder materials now include thermoplastic and thermosetting resins, metals, ceramics, and metal salts. Soft metals, metallic oxides, metallic sulfides, metallic selenides, metallic tellurides, and many others are currently under careful consideration as solid lubricants by a large number of research groups [2].

3. SOLID LUBRICANTS

General description: bearings used under vacuum, at very high temperatures or under very high radiation cannot be lubricated by liquid lubricants or greases. For these and many other cases, solid lubricants are used, deemed to be any solid material used to reduce friction and wear between two moving surfaces.

In general, the solid material is interposed as a film between sliding and /or rolling surfaces. Simply stated, an adequate solid material is required for the special lubrication requirements of extreme operating conditions, such as very high or very low temperatures over a wide range, e.g. -200 to 850^{o}C, and corrosive atmospheres. Such materials normally have a layered crystalline structure which ensures low shear strength, thereby minimizing friction. The shear strength between the crystalline layers is weak and sets up a low and sets up a low friction mechanism by slippage of the crystalline layers under low shearing forces. Examples of layer lattice solids are molybdenum disulphide, graphite, boron nitride, cadmium iodide and borax. Solid lubricants are used mainly in the form of powders or as bonded solid films.

A good solid film lubricant has strong adhesion to the bearing substrate material, full surface coverage and good malleability. It should also be chemically stable and prevent corrosion, taking into account operational and environmental conditions. Many solid film lubricants have poor wear resistance, since any breaks in the film are not self-healing, in contrast to the surface coating formed by a liquid lubricant. Advanced solid film lubricants perform reliably in many specific applications and much experience has been gained to better understand their limitations. The most commonly used disulphide, graphite, polytetra fluroethylene propylene.

Another group of materials, the self-lubricated materials, are related to solid lubricants and are particulary important for bearings. Their self-lubricating characteristics eliminate the need of grease or other lubrication and give improved performance under high temperature conditions. Graphalloy (Graphite/metal) alloys make use of special properties of graphite, the structure of which can be compared to a deck of cards with individual layers able to easily slide off. This phenomenon gives the material a self lubricating ability matched by few other materials and allows for the elimination of grease or oil that would evaporate, congeal or solidify, causing premature failure. The graphite matrix can be filled with a variety of embedded lubricants to enhance chemical, mechanical and tribological properties to give a constant, low friction coefficient rather than just a surface layer, helping to protect against catastrophic failure. Lubrication is maintained during linear motion where lubricant is not drawn out and dust is not pulled in.

A recent development in solid bearing lubricants is micro –porous polymeric lubricants, MPL, where a polymer containing a continous microporous network has oil contained within the pores, which may include appropriate additives. The oil content in the polymer can be more than 50% by weight and the microporous polymer acts as a sponage, releasing and absorbing oil when necessary [3].
Main methods of application for solid lubricants include the following:

1) Mixing with fats and fatty oils
    i) Dispersed in oils or suspension
    ii) Added to grease
2) Dry coating
    i) Solid lubricants dispersed in vehicles are coated or sprayed on solid surfaces, and then dried.
    ii) Sputtering: In a vacuum, solid lubricants such as molybdenum disulfide are placed at the cathode and bombarded by inert gas ions to accumulate ejected particles on solid surfaces for coating.

iii) Ion plating: In a vacuum, the plating material (such as gold or silver) is ionized and accelerated by an electric field to deposit a metal coating.

3) Composite materials: Used to fill the surface irregularities of resins and ceramics.
4) Solid lubricants are applied directly to sliding surfaces [4].

Table 1 Classification of solid lubricants [4].

TYPE	EXAMPLES
Metals and Inorganic Components Layered Structure compounds Non- Layered compounds Soft Metals	Molybdenum disulfide, graphite, boron nitride PbO, CaF2 Pb, Sn, Au, Ag, Cu
Organic compounds Soaps, fats, waxes Polymers Malleable substances	Beef tallow, lithium stearate, bee wax Polytetrafluoroethylene (PTFE), polyimide Phthalocyanine

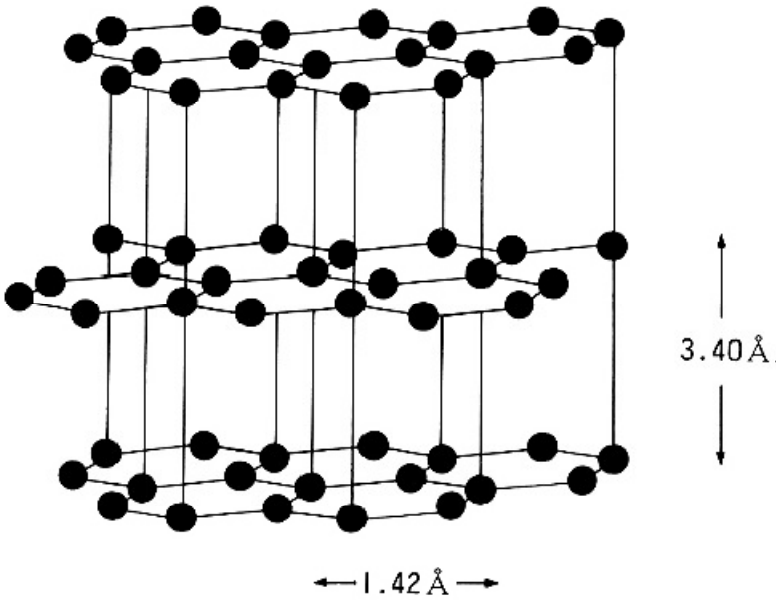

Figure 1 Crystalline Structure of Graphite [4].

3.1. Inorganic Lubricants

Conventional organic lubricants fail rapidly in the high vacuum of space because of volatilization of organic components. This difficulty has been avoided by the use of inorganic solid film lubricants comprising various combinations of lubricating materials dispersed in an inorganic binder. These compositions are applied and bonded to the mating surfaces as a thin solid film. The binder usually forms a matrix and holds the lubricant particles in many tiny reservoirs. One previously known composition of this type employs molybdenum disulfide, graphite and gold as lubricating materials and sodium silicate as the binder. This composition presents disadvantages in that the sodium silicate is unstable in the presence of moisture, and the wear life is shortened by disruption of the film. Improved moisture resistance has been obtained by using potassium silicate, either by itself or modified with sodium fluoride, as the binder in place of sodium silicate, but the wear life is still too short for many applications. A more effective binder material is thus needed to obtain a longer wear life, consistent with other favorable characteristics [5].

3.2. Organic Lubricants (PTFE)

Polytetrafluoroethylene (PTFE) is an important polymer based engineering material. When rubbed against a hard surface, PTFE exhibits a low coefficient of friction but a high rate of wear. It is white or gray in color. It is an ideal bearing material for heavy and light load pressures with medium and low surface speeds. PTFE has all qualities of bearing alloy like compatibility, conformability, embedability, load capacity, fatigue strength, corrosion resistance and hardness. The low-friction characteristics of PTFE are largely responsible for the inception of this paper.

PTFE is a popular polymer solid lubricant because of its resistance to chemical attack in a wide variety of solvents and solutions, high melting point, low coefficient of friction, and biocompatibility. It is commonly used in bearing and seals applications. Unfortunately, PTFE suffers from poor wear resistance [2]. Because of the relative softness of PTFE, it is logical to expect that its load-carrying ability and its wear resistance might be improved by the addition of suitable fillers. Accordingly, several fillers are tried by researchers in combination with this plastic, including graphite, molybdenum disulfide, fiber glass, carbon ,bronze, dental silicate, silicon, titanium dioxide, silver, copper, tungsten and molybdenum[6].

Recently, there have appeared publications looking at the tribological worthiness of nanocomposites made with epoxies, which in its neat form is a notoriously poor tribological performer. Silica, alumina, and silicon nitride nanoparticles have all been incorporated into epoxies with most additions improving both the coefficient of friction and wear resistance. There is also work that has incorporated fluorinated polyaryletherketone into epoxy to create a polymer/epoxy blend that, in the main, shows roughly 20% reductions in friction coefficient. As mentioned above, PTFE has also been used as filler in epoxy matrixes [7].

Table 2 The most used solid lubricants and their characteristics [8].

Solid lubricant	Characteristics
MoS2	MoS2 has a low coefficient of friction both in vacuum and atmosphere, and it does not rely on adsorbed vapors or moisture. Its thermal stability in non oxidizing environments is acceptable to 1373 K, but in air the temperature limitation of MoS2 may be reduced to a range of 623 to 673 K by oxidation. Adsorbed water vapors and oxidizing environments may actually result in a slight, but insignificant, increase in friction. MoS2 has greater load-carrying capacity than other commonly used lubricants, such as graphite and PTFE. MoS2 has a hexagonal crystal structure with the intrinsic property of easy shear. The lubrication performance of MoS2 often exceeds that of graphite, and MoS2 is effective in vacuum where graphite is not.
Graphite	Graphite has a low coefficient of friction and very high thermal stability (2273 K and above). Graphite has a hexagonal crystal structure with the intrinsic property of easy shear, although graphite relies on adsorbed moisture or water vapors to achieve low friction. Use in dry environments, particularly in vacuum, may be limited. At temperatures as low as 373 K, the amount of water vapor adsorbed may be reduced to the point that low friction cannot be maintained, so sufficient water vapor may be deliberately introduced to maintain low friction. Practical application at high temperatures is limited to a range of 773 to 873 K because of oxidation. When necessary, additives composed of inorganic compounds may be added to enable use at temperatures to 823 K.
PTFE	PTFE has a low coefficient of friction both in vacuum and atmosphere because of a lack of chemical reactivity. PTFE does not rely on adsorbed vapors or moisture. It possesses low surface energy and does not have a layered structure. The macromolecules of PTFE slip easily along each other, similar to lamellar structures. Practical application temperatures range from 173 to 523 K. PTFE does not have greater load carrying capacity and durability than other alternatives. The low thermal conductivity of PTFE inhibits heat dissipation, which causes premature failure due to melting and limits use to low-speed sliding applications where MoS2 is not satisfactory. PTFE shows one of the smallest coefficients of static and dynamic friction, down to 0.04. Operating temperatures are limited to about 523 K.
Soft metals	Lead, gold, silver, copper, indium, and zinc possess relatively low coefficients of friction both in vacuum and atmosphere because of their low shear strengths. These metals are extremely useful for high temperature applications up to 1273 K and for rolling element applications, such as roller bearings, where sliding is minimal.

Table 3 Advantages and Disadvantages of Solid Lubricants [8].

ADVANTAGES	DISADVANTAGES
• Are highly stable in high-temperature, cryogenic temperature, vacuum, and high-pressure environments. • Have high heat dissipation with high thermally conductive lubricants, such as diamond films. • Have high resistance to deterioration in high-radiation environments. • Have high resistance to abrasion in high-dust environments. • Have high resistance to deterioration in reactive environments. • Are more effective than fluid lubricants at intermittent loading, high loads, and high speeds. • Enable equipment to be lighter and simpler because lubrication distribution systems and seals are not required. • Offer a distinct advantage in locations where access for servicing is difficult. • Can provide translucent or transparent coatings, such as diamond and diamond like carbon films, where desirable.	• Have higher coefficients of friction and wear than for hydrodynamic lubrication. • Have poor heat dissipation with low thermally conductive lubricants, such as polymer-base films. • Have poor self-healing properties so that a broken solid film tends to shorten the useful life of the lubricant (However, a solid film, such as a carbon nanotube film, may be readily reapplied to extend the useful life.) • May have undesirable color, such as with graphite and carbon nanotubes.

4. CONCLUSION

The current review presented the different types of solid lubricants. The technology of solid lubrication has advanced rapidly in the past few decades, primarily in response to the needs of the aerospace and automobile industries. Solid lubricants are used where the containment of liquids is a problem and when liquid lubricants do not meet the advanced requirements. Under high vacuum (such as in space), high temperatures, cryogenic temperatures, radiation, dust, clean environments, or corrosive environments, and combinations thereof, solid lubrication may be the only feasible system. The materials designed for solid lubrication must not only display desirable coefficients of friction (0.001 to 0.3) but must maintain good durability in different environments, such as high vacuum, water, the atmosphere, cryogenic temperatures, high temperatures, or dust. Therefore, the successful use of materials and coatings as solid lubricants requires understanding their material and tribological properties and knowing which solid lubricant formulation is best for a chosen application. Issues such as substrate surface pretreatment, materials and coatings compatibility, the mating counterpart material, and potential debris generation must be taken into account during the design of a lubricated device or of moving mechanical assemblies.

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